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(54) Title: METHOD FOR INHIBITING SOLIDS FORMATION AND BLENDS FOR USE THEREIN

(57) Abstract

Gas hydrate or ice formation is inhibited or retarded by adding to a medium or surface susceptible thereto such as a pipeline containing gas and water at least one additive which is at least one of (i) an amino acid or derivative thereof, (ii) an amino alcohol or derivative thereof, (iii) a glycol ether or derivative therof, (iv) a hydroxy acid or derivative thereof, and (v) a corrosion inhibitor especially at least 2 such additives and in particular with a polymer of a polar ethylenically unsaturated compound such as PVP.

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METHOD FOR INHIBITING SOLIDS FORMATION AND BLENDS FOR USE THEREIN

The present invention relates to a method for inhibiting the formation of solids, in particular hydrates and/or ice especially in the petroleum and natural gas industries.

Hydrates are formed of two components, water and certain gas molecules, e.g. alkanes of 1-4 carbons, especially methane and ethane, such as those found in natural gas. These 'gas' hydrates will form under certain conditions, i.e. when the water is in the presence of the gas and when the conditions of high pressure and low temperature reach respective threshold values. The gas may be in the free state and/or or dissolved in a liquid state, for example, as a liquid hydrocarbon.

The formation of such hydrates can cause problems in the petroleum oil and natural gas industries.

Hydrate formation in the field may cause blocked pipelines, valves and other process equipment.

The problem is particularly of concern as natural gas and gas condensate resources are discovered where operating conditions surpass these threshold values, i.e. in deep cold water and on-shore in colder climates.

Hydrates can also form in association with the underground hydrocarbon reservoir thus impeding production by blockage of reservoir pores.

The problem of hydrate formation is however commonest during gas transportation and processing, the solid hydrate precipitating from moist gas mixtures. This is particularly true with natural gas

which when extracted from the well is normally saturated with water. Often in such a case, in a cold climate, hydrates will form in downstream transportation networks and this can cause large pressure drops throughout the system and reduce or stop the flow of natural gas.

Hydrate formation may also occur during natural gas cryogenic liquefaction and separation.

A typical situation where hydrate formation can occur is in offshore operations where produced fluids are transported in a long vertical pipeline, for example, a riser system. Such produced fluids normally include light gases known to form hydrates and water. In such a situation a temperature of at most 4.5°C and a pressure of at least 1. MPa (150 psi) would be sufficient for hydrate formation.

Several methods are known to prevent hydrate formation and subsequent problems in pipelines, valves and other processing equipment.

Physical methods have been used, e.g. increasing gas temperature in the pipeline, drying the gas before introduction into the pipeline, or lowering the gas pressure in the system. However, these techniques are either expensive or are undesirable because of loss of efficiency and production.

Chemical procedures have also been used. Electrolytes, for example, ammonia, aqueous sodium chloride, brines and aqueous sugar solutions may be added to the system.

Alternatively, the addition of methanol or other polar organic substances, for example, ethylene glycol or other glycols may be used. Methanol injection has been widely used to inhibit hydrate formation. However, it is only effective if a sufficiently high concentration is present since at low concentrations there is the problem of facilitation of hydrate formation. Also for methanol to be used economically under cold environmental conditions there must be early separation and expulsion of free water from the well in order to minimise methanol losses in the water phase.

In addition there are problems of ice formation, e.g. in the petroleum and natural gas industries. During the exploration and

production of oil and gas in the colder areas of the world, for example Alaska, pipelines and associated equipment such as valves are also susceptible to damage due to ice formation. Ice can also form in pipelines containing water and oil/or gas usually at temperatures of less than 0°C, depending on the gas pressure hydrates may or may not also form in the pipeline. Again at present substantial amounts of methanol, ethanol or mono, di or triethylene glycol are used to stop such ice formation.

Furthermore during winter, serious problems can arise on surfaces which are susceptible to the formation of ice and snow. Roads, walkways, railway points, runways and taxiways are all prone to the hazards of ice formation. It is also very important that aircraft surfaces are maintained free of ice.

It is a major exercise for local authorities and airports to reduce the delay or risk of accident caused by such adverse weather conditions and to provide a maintenance service for these areas which will allow the safe movement of traffic and the general public.

Car windscreens are also prone to icing during the winter months and it would be advantageous to be able to prevent ice formation.

Ice formation may also lead to damage in the outdoor storage and transportation of particulate material, for example, coal.

Crops and outdoor plants are also susceptible to damage during winter conditions.

It is known to use deicing compositions to treat surfaces which have become prone to ice formation. Suitable chemicals which have been used include sodium chloride and glycol based formulations.

Such deicing chemicals are primarily employed as a curative measure after the ice has formed. It would be particularly advantageous to be able to inhibit the formation of ice on susceptible surfaces as a preventative measure.

We have now found certain additives which may be used as effective hydrate or ice inhibitors at low concentrations.

Thus, according to the present invention, there is provided a method for inhibiting or retarding hydrate or ice formation, which

method comprises adding an additive (hereinafter called the Additive) which is at least one of (i) an amino acid or derivative thereof, (ii) an amino alcohol or derivative thereof, (iii) a glycol ether or derivative thereof (iv) a hydroxy acid or a derivative thereof, and (v) a corrosion inhibitor, the Additive being added in an amount effective to inhibit or retard hydrate or ice formation, to a medium susceptible to hydrate or ice formation, with the proviso that Additives (i) which are of Formula II below are not added as sole Additives or in admixture as sole other Additive with Additive (v).

The Additive (i)-(iv) (and often v) is usually at least difunctional, e.g. with 2-4 functional groups. It preferably has a structure including an oxygen atom in an ether group or hydroxyl group and at least one of another oxygen atom in an ether or keto group and a nitrogen atom in an amino group, said O and N and/or O atoms being spaced by 1-6, preferably 2-5, especially 2 or 3 carbon atoms, which may be in an aliphatic, cycloaliphatic or aromatic group.

The Additive (i) may be an amino acid or derivative thereof, in particular one with at least one asymmetric carbon atom; the Additive may be in the racemic form, but is preferably optically active, i.e. in D or especially L-form. The Additive (i) may be in the form of the free carboxylic acid (including a carboxylic anion form, e.g. as a sodium or potassium salt) or as a derivative of said carboxylic acid, e.g. as an amide (e.g. with ammonia or with a primary amine which may or may not be a hydroxy organic amine) or hydrazide (e.g. with hydrazine) or an ester, e.g. as an alkyl ester, e.g. with 1-6 carbons such as a methyl or ethyl ester, or a hydroxyalkyl ester, e.g. with 1-6 carbons such as hydroxymethyl, 1 or 2 hydroxyethyl, 2 or 3 hydroxypropyl ester. The amino acid (or derivative) is preferably an alpha amino carboxylic acid, especially with the amino and carboxylic acid groups bonded to an aliphatic carbon atom, especially a -CH- group. The amino group in the amino acid may also be in a non alpha position relative to the acidic group, e.g. in a beta, gamma or delta position, especially terminal on an alkyl, phenyl or phenylalkyl group attached to the acidic group; examples

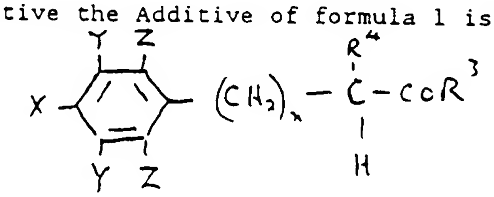
are omega amino alkanoic acids such as 4-amino butyric acid and p-amino phenyl acetic acid. Iminodiacetic and N-hydroxy methyl iminodiacetic acid may also be used. The Additive may contain an amino group in NH_2 or NH_3 form (whether as a salt, e.g. hydrochloride or hydrobromide or zwitter ion form) or an N-acyl derivative thereof, such as with an alkanoic acid, e.g. of 1-10 carbons such as acetic acid, or an aromatic acid, e.g. of 6-16 carbons such as benzoic acid or a carbonate half ester such as a monoalkyl carbonate, e.g. mono tert butyl carbonate or an aromatic or aralkyl carbonate, e.g. phenyl carbonate or benzyl carbonate. Derivatives of the amino acid with an N-hydroxy alkyl group, e.g. of 1-4 carbons, e.g. 1 or 2 carbons such as hydroxymethyl may also be used; such derivatives may also involve an NH ring in which the hydroxy l and acid groups are substituents as in hydroxy proline. Examples of such amino acid derivatives with an N-hydroxy alkyl group are N-sulphoalkyl and N-carboxyalkyl derivatives of Additives (ii) as further described below; such compounds may be 1, 2 or 3 sulphoalkylene or especially 1,2 or 3 carboxyalkylene derivatives, especially linear alkylene derivatives. Especially preferred are those derivatives which are N-derivatives of a tris(hydroxyalkyl) alkylamine, in particular tris(hydroxymethyl) methylamine, such as N-[(tris hydroxymethyl)methyl] glycine.

The Additive (i) is however preferably of formula (I) R-$CH(NH_2)COOH$ (or a derivative thereof), wherein R represents hydrogen or an aromatic, aralkyl, heterocyclic, heterocyclic aliphatic, cycloaliphatic or aliphatic group. The aromatic group preferably has 6-20 carbons, e.g. 6-10 carbons, such as phenyl optionally substituted by amino, hydroxyl carboxylic or alkyl, e.g. of 1-6 carbons such as methyl or ethyl or alkoxy, e.g. of 1-6 carbons such as methoxy or ethoxy. The aralkyl group preferably comprises an aromatic group as described above and the alkyl part of the aralkyl group preferably has 1-4 carbons such as methyl or 1 or 2 ethyl. The heterocyclic ring in the heterocyclic or heterocyclic alkyl group may be a nitrogen heterocyclic ring with 1-3 ring nitrogens as in a 1,3-imidazole ring. The cycloaliphatic group may have 5-8 carbons, e.g. cyclohexyl or cyclopentyl. The group R is especially an aliphatic

group e.g. of 1-6 carbon atoms, in particular a saturated hydrocarbyl group, e.g. linear or branched and optionally substituted, especially in a terminal position in the hydrocarbyl group by at least one of a hydroxyl, alkoxy, mercapto or alkyl thio group, e.g. with 1-6 carbons, especially 1 or 2 carbons in the alkoxy and alkyl thio group, or an amino group, e.g. of formula $-NR^1R^2$, wherein each of R^1 and R^2 which may be the same or ifferent represents hydrogen or alkyl of 1-6 carbons such as methyl or ethyl, or may be an $NHC = NH-(NH_2)$ group (as such or in a salt form) or a ureido or carboxylic acid group or ester (e.g. alkyl or hydroxyalkyl ester) or hydrazide or amide thereof.

Thus the amino acid which is the Additive (i) or from which it is derived, may be a basic amino acid with 2 or 3 amino groups and 1 carboxylic acid group, such as ornithine, lysine, arginine or guanidine or histidine, especially in its L-form, or an acidic amino acid with 2 or 3 carboxylic acid groups and 1 amino group, such as glutamic or aspartic acid or amide, especially in its L-form. Most preferably, however, the amino acid, which the Additive (i) is or from which it is derived, has 1 amino and 1 carboxylic group (or derivative thereof) especially one of formula I, in which R is alkyl or hydroxyalkyl, alkoxyalkyl, mercaptoalkyl or alkylmercaptoalkyl group or in the case of mercaptoalkyl groups (as in cysteine) the corresponding disulphide (as in cystine); such amino acids are preferably in their L forms. The Additive is thus preferably serine, threonine, valine, leucine, isoleucine, homoserine, methionine, cysteine or cystine; L-serine is preferred.

When used alone or in the presence of a corrosion inhibitor as sole other additive the Additive of formula 1 is not of formula II



where R^3 is OH, OCH_3, OC_2H_5, $NHNH_2$ or H, R^4 is NH_2 or NH_3, each of X, Y and Z is hydrogen or OH and n is a number in the range 0 to 6, or a polymer thereof when R^3 is NH_2. Thus except in mixtures with an

Additive (i)-(iv) phenylalanine and tyrosine and their carboxylic acid derivatives are preferably excluded. However, there may be used compounds of formula II, wherein at least one of X, Y and Z represents an alkoxy, acyloxy, keto, amino or carboxyl group such as an alkoxy group of 1-6 carbons, e.g. methoxy or ethoxy, or acyloxy such as aliphatic acyloxy, e.g. of 1-10 carbons such as acetoxy, or keto as in alkylketo with 2-6 carbons, e.g. CH_3CO-. Advantageously, however, in the additive of formula I, group R does not comprise an aromatic group.

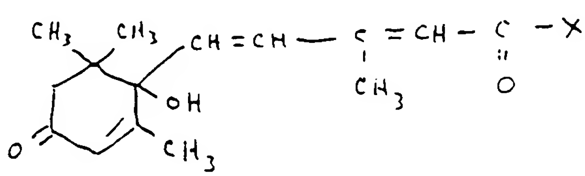
The amino acid may also be an amino sulphonic acid, e.g. with an aliphatic group, e.g. of 1-10 carbons, aromatic group, e.g. of 6-16 carbons or cycloaliphatic group, e.g. of 5-7 carbons, to which the amino and sulphonic groups are attached. Taurine and amino benzene sulphonic acid may be used.

The Additive (ii) may also be an hydroxyamine, which is usually an aliphatic compound with 2-10 carbon atoms, especially 3-6 carbon atoms, in particular a saturated aliphatic compound. The Additives (ii) may contain 1-5 hydroxyl groups, e.g. 1, 2 or 3 hydroxy groups and 1-3 amino groups, e.g. 1 or 2 amino groups, which may be of formula NR^1R^2, where R^1 and R^2 are as defined above. The Additive (ii) may be a secondary or tertiary amine, but is preferably a primary amine, e.g. with 1 NH_2 group, and with 1-3 hydroxyl groups and has especially an alkane group, which may be linear or branched, substituted by such amino and hydroxyl groups which are preferably attached to adjacent carbon atoms. The hydroxyamine may be used as such or in the form of a salt with an inorganic acid, e.g. hydrochloric acid or an organic acid, e.g. an aliphatic mono or di carboxylic acid such as one with 1-10 carbon atoms, e.g. acetic or propionic acid or maleic or oxalic acid. Examples of such Additives (ii) are tris-(2 hydroxyethyl) amine, tyrosinol or valinol (e.g. the L isomer) and especially tris-hydroxymethyl-methylamine $(HOCH_2)_3CNH_2$ and its corresponding ammonium chloride salt.

The Additive (iii) may also be an ether, which contains at least 1 such as 1-6 ether oxygen atoms and 0-6, e.g. 1 oxygen atoms in a hydroxyl group, the number of ether oxygen atoms being

preferably at least the same as and especially 0-3 more than the number of hydroxyl oxygen atoms. Preferably the Additives (iii) are glycol ethers, derived structurally from a diol, e.g. an aliphatic diol of 2-4 carbon atoms such as ethylene glycol or 1,3-propylene glycol, or structurally from a self condensate thereof, e.g. di or triethylene glycol, or mixtures of said diols. One or both hydroxyl groups from such diols (or condensate thereof) may be etherified, e.g. with an alkyl group such as one with 1-10 carbons, e.g. methyl, ethyl, n-propyl or n-butyl. Preferably such Additives (iii) are the reaction products of an alkanol with ethylene oxide and/or propylene oxide. One or more hydroxyl groups in the ether may be acylated, e.g. with an aliphatic or aromatic acyl group with 1-10 or 6-16 carbon atoms respectively such as acetyl or benzoyl. Examples are 2-butoxyethanol (monobutyl glycol ether) and $2(2^1$-butoxy ethoxy) ethanol (mono butyldiethylene glycol ether) and their corresponding acetates.

The Additive (iv) is a hydroxy acid (especially a hydroxy carboxylic acid) which may be an aliphatic, aromatic, cycloaliphatic, cycloaliphatic-aliphatic or araliphatic compound with 1-20, 6-20, 5-7, 5-25 or 7-20 carbon atoms respectively. Preferably the aliphatic hydroxy acid is an alpha hydroxy acid, e.g. of 2-6 carbons such as glycollic, lactic or citric acid, while the aromatic and araliphatic acids may be salicylic, p-hydroxybenzoic or 2-(p-hydroxyphenyl) propionic acid. Derivatives of the additive (iv) on the carboxyl group may be used such as salts, e.g. with alkali metals, esters, amides or hydrazides, in particular when the additive (iv) contains at least one group -COX where X is as defined below. However, preferably the hydroxy acid is a cycloaliphatic-aliphatic compound, especially one with at least one of a keto and an olefinic unsaturated group, in particular abscisic acid or a derivative thereof of formula



wherein X represents OR^5, wherein R^5 is hydrogen or alkyl, e.g. of 1-6 carbons optionally hydroxy substituted, such as methyl, ethyl or 2-hydroxyethyl, or X represents amino (e.g. NH_2) or hydrazido (e.g. $NHNH_2$).

All isomers of the aforementioned abscisic acid derivatives may be suitable for use in the method of the present invention. A preferred compound for use in the present invention is (+/-)-2-cis,4-trans abscisic acid.

The additive (v) is a corrosion inhibitor, e.g. for steel and usually one suitable for use in anaerobic environments, and is especially a nitrogenous one with 1 or 2 nitrogen atoms. The corrosion inhibitor may be a primary, secondary or tertiary amine, or a quaternary ammonium salt, usually in all cases with at least one hydrophobic group, usually a benzene ring or a long chain alkyl group; the inhibitor preferably has surfactant activity and especially surface wetting activity. It may be a quaternary ammonium salt, a long chain aliphatic hydrocarbyl N-heterocyclic compound or a long chain amine. The quaternary salt may be an (optionally alkyl substituted) benzyl trialkyl ammonium halide, in particular when at least 1 and especially 1 or 2 alkyl groups is of 1-20, in particular 8-20 carbons such as cetyl and the other alkyl groups are of 1-6 carbons such as methyl or ethyl; examples are benzyl alkyldimethyl ammonium chloride and Benzalkonium chlorides. The aliphatic hydrocarbyl group in the heterocyclic compound usually has 8-24 carbons in the hydrocarbyl group, preferably a linear saturated or mono or diethylenically unsaturated hydrocarbyl group; cetyl-, stearyl and especially oleyl- groups are preferred. The N-heterocyclic compound usually has 1-3 ring N atoms, especially 1 or 2 which usually has 5-7 ring atoms in each of 1 or 2 rings; imidazole and imidazoline rings are preferred. The heterocyclic compound may have the aliphatic hydrocarbyl group on an N or preferably C atom in the ring; the ring may also have an amino-alkyl (e.g. 2-amino ethyl) or hydroxyalkyl (e.g. 2-hydroxyethyl) substituent, especially on an N atom. N-2-aminoethyl-2-oleyl-imidazoline is preferred. The long chain amine usually contains 8-24 carbons and preferably is an

aliphatic primary amine, which is especially saturated or mono ethylenically unsaturated, an example is dodecylamine.

Mixtures of Additives of the same type (i), (ii), (iii), (iv) or (v) may be used, but also mixtures of different types (i), (ii), (iii), (iv) and/or (v), especially mixtures of (v) and at least one of (i), (ii), (iii) and (iv). The mixtures may contain at least 1%, but preferably at least 10% and not more than 90% of each Additive, especially in the form of two component mixtures with 25-75; 75-25 ratios of the two components which are in particular mixtures of (i) and (iii). Such mixtures form another aspect of the invention, so there is also provided a blend which comprises a mixture of at least two Additives (i), (ii), (iii), (iv) and/or (v) apart from mixtures consisting solely of an Additive of Formula II and (v); such blends are primarily for use as gas hydrate and/or ice inhibitors.

Additives (i-iv) of the present invention for use as hydrate or ice inhibitors are preferably water soluble, e.g. to at least 10 g/l in water at 20°C. They may be used undiluted, but preferably are in solution such as aqueous solution, for example, as a solution in brine, or preferably an alcohol, for example, a water miscible one such as methanol or ethanol. Preferably are used Additives i-iv, an aqueous solution of which has a pH 1.5-12, e.g. 4-9, either naturally or after adjustment of the pH. Additives (v) are preferably used in alcoholic solution.

The Additive(s) is suitably injected at concentrations in the range 10 to 200,000 or 10 to 20,000 ppm, e.g. 30 to 10,000 ppm, especially 50-1200 ppm based on the total water volume in the medium, in which hydrate or ice formation is to be inhibited, in particular at concentrations in the range 100-700 ppm. The amount of methanol, ethanol, or mono, di or tri ethylene glycol added relative to the total water volume in the medium is usually less than 10%, e.g. less than 5% or 2%, but especially less than 10,000 ppm.

The inhibitors may be injected at normal ambient conditions of temperature and pressure.

For use as ice inhibitors they may be applied in the form of a spray or aerosol. They may be applied as a coating in combination

with a suitable carrier material or thickening agent.

It has also been found that blends of at least one Additive and a polymer of a polar ethylenically unsaturated compound can give synergistic results compared to the ingredients above, so that blends of at least one Additive and a polyvinyl pyrrolidone, had a gas hydrate inhibition time in a test very many more times than each individually, e.g. at least two times more than the sum of their individual times.

The Additives may thus also be used in formulations which also comprise a polymer of a polar ethylenically unsaturated compound; these Formulations constitute another aspect of the invention.

The polymer of the polar ethylenically unsaturated compound is usually water soluble (to at least 10 g/l at 20°C) and advantageously has a molecular weight of 1000-1500,000, e.g. 5000-1,000,000, preferably 200,000-1,000,000 and especially 400,000-900,000. The ethylenically unsaturated compound is preferably a vinyl or methyl vinyl group, and the polar group may be an alcohol, carboxylic acid, sulphonic acid or N-heterocyclic group, especially pyrrolidone. Preferred polar compounds are thus vinyl sulphonic acid, acrylic and methacrylic acids and N-vinyl pyrrolidone and "vinyl alcohol". The polymers may be copolymers, but are preferably homopolymers of these polar compounds, especially polyvinyl alcohol (e.g. hydrolysed polyvinyl acetate), polyacrylates and polyvinyl pyrrolidone. The amount of said polymer is usually 10-1000%, such as 50-300% or 90-250% based on the weight of the total of Additive(s).

Formulations may be used in amount of 50-10,000 ppm, especially 150-2000 ppm, e.g. 500-1500 ppm relative to the total water in the medium in which hydrates or ice may form (including any water added in the formulation). The formulations may comprise the corrosion inhibitor (Additive (v)) and the polymer as well as the Additive (i-iv), which are then preferably in the weight ratio 5-200:100-2000:100-2000, especially 10-100:400-800:150-500 or as percentages of the total formulation weight of corrosion inhibitor, polymer and Additive (i-iv) of 1-20%, 40-80% and 10-50% respectively, especially 1-10%, 50-70% and 20-40% respectively. In the Formulation, Additive

v is usually present in an amount of 0.1-50% by weight of the total of Additives (i-iv), e.g. 1-25%, especially 5-20%.

The Formulation may also contain another hydrate or ice inhibitor and/or a water dispersant or surfactant, in particular an anionic one such as sodium dodecyl sulphonate or stearic acid and in amount of 1-10% of the Formulation weight and/or a biocide, e.g. formaldehyde, e.g. in amount of 10-10,000 ppm and/or a metal complexant such as citric acid (e.g. in amount of 10-10,000 ppm) all amounts being in relation to the total weight of the Formulation.

The Formulations may be used to retard or inhibit hydrate or ice formation in the same manner as the individual Additives, as described above.

The inhibitor Additives and Formulations of the present invention are suitable for use in media containing water and gas, in particular in the petroleum, natural gas and gas industries.

In particular, they may be suitable for use during the transportation of fluids comprising gas and water. They may also be suitable for use in oil based drilling muds to inhibit hydrate formation during drilling operations.

In another aspect therefore the invention provides an oil based drilling mud, which comprises as hydrate inhibitor at least one Additive, as such or in a Formulation.

When used during the transportation of fluids, e.g. gases in pipelines the inhibitors may be injected continuously or batchwise into the pipeline upstream of conditions wherein hydrate formation may occur.

In drilling operations the inhibitors may be added to the drilling muds in the mud tank at the wellhead.

The Formulations may be used to retard or inhibit ice formation.

In use against ice the material of the present invention may suitably be used on surfaces which are particularly susceptible to ice formation. Typical surfaces include airport runways, taxiways, roads, walkways, windscreens and aircraft, especially the main wings thereof.

Suitable media include bulk solutions, for example, storage tanks. Other suitable media are cooling systems, for example, radiators for motor vehicles.

The method of the present invention may be primarily used before the surface or medium is exposed to a freezing environment as a method of protection against the formation of ice on the surface or in the medium.

The ice inhibitors of the present invention may be used alone or with other ice preventative chemicals.

For example, they may be used with deicing chemicals such as those disclosed in European patent application EP 375214. This discloses a deicing composition comprising an aqueous solution of an alkali metal acetate and/or an alkali metal formate, an alkali metal phosphate and an alkali metal nitrite.

It will be understood by those skilled in the art that the ice inhibitors of the present invention may be used in conjunction with ice dispersants and other conventional additives.

The invention is illustrated in the following Examples.

Examples

To assess the efficiency of hydrate inhibitors suitable for use in the method of the present invention, tests were carried out using the following procedure:

The hydrate inhibitor test apparatus consisted of a simple 316 stainless steel pressure cell, with a usable internal volume of 1000 cm^3 with a thermostated cooling jacket, a sapphire window, an inlet and outlet and a platinum resistance thermometer. The cell contained water which was stirred by a magnetic pellet. Temperature and pressure were monitored and the results provided on a computer data logger; gas hydrates were also detected visibly using a time lapse video recording system. Before each test the cell was cleaned thoroughly by soaking successively in 10% aqueous hydrochloric acid for 1 hour, 10% aqueous sodium hydroxide solution for 1 hour and then double distilled water.

Into the cell was placed 200 cm^3 of pre-chilled double distilled water with or without the chemical to be tested. A PTFE

stirrer pellet was then placed in the cell and the pH of the solution measured with subsequent adjustment if desired by the addition of small but concentrated amounts of hydrochloric acid or sodium hydroxide. After sealing the cell the water was then stirred at 450 rpm and allowed to cool to the operational temperature of 2°C. When this temperature was reached the stirrer was stopped and the video recorder started. Methane was then admitted to the cell until the pressure reached 70 bar and the temperature, pressure and time were noted. The stirrer was restarted to run at 450 rpm and the time noted. Hydrates were observed to form in the vessel when the solution in the vessel turned opaque, coincident with which was a sharp temperature increase of about 0.2°C and a gradual pressure reduction. The time from first contact of water and gas to formation of hydrate was read from the logger.

The experimental conditions are a very severe and accelerated test of gas hydrate formation and inhibition.

Example	Additive	Concentration ppm	pH	Inhibition Time (mins)
A	None	-	-	6-8
1	L-arginine	200	2.5	14
2	L-arginine	200	4.5	18
3	L-arginine	200	10	14
4*	L-cystine	400	2	19
5	L-histidine	200	2.0	14.5
6	L-histidine	400	2.2	12.5
7*	L-leucine	200	2.5	26.5
8	L-leucine	400	2.2	15
9*	L-methionine	600	1.8	31
10*	L-methionine	800	1.8	46
11	L-serine	1000	2.0	13.5
12*	L-serine	400	2.5	35.5
13	Taurine	400	2.5	12
14*	Tris***	400	2.2	34
15	Tris***	400	9.5	10
16	Tris*** maleate	400	4.2	11
17	Tris*** maleate	1000	4.0	11
18	L-valinol	400	2.2	14
19	Abscisic acid	400	3.5	20
20	3-[4 hydroxyphenyl]	400	3.5	10
	propionic acid**	1000	3.3	14
21	Tris glycine****	400	5.0	16

In the above Table

* denotes experiments with a stirring speed of 500 rpm

** denotes an experiment with a cell water temperature of 2.1ºC

*** Tris denotes tris(hydroxymethyl) methyl amine

**** Tris glycine denotes N-tris(hydroxymethyl)methyl glycine

Examples B, 22 and 23

The process of Examples A and 1-21 was repeated with tris(hydroxymethyl) methyl ammonium chloride and the same conditions apart from a 50 bar pressure of methane. The results were as follows.

Example	Conc. of Additive ppm	pH	Inhibition Time
B	0	-	11
22	400	5.5	15
23	600	5.5	71

Examples C and 24-28

The process of Examples A and 1-21 was repeated with various ether additives and the same conditions apart from a 4°C cell water temperature and 500 rpm stirring speed. The results were as follows.

Example	Additive	Concentration ppm	pH	Inhibition Time (mins)
C	-	-	-	6
24	BDGA	600	4.5	18
25	BGE	600	4.5	43
26	BGE	1200	4.05	43
27	BDGE	600	4.2	42
28	BGA	600	4.4	18

BDGA denotes diethylene glycol mono n-butyl ether mono acetate

BGE denotes ethylene glycol mono n-butyl ether

BDGE denotes diethylene glycol mono n-butyl ether

BGA denotes ethylene glycol mono n-butyl ether mono acetate

Examples 29-35

The process of Example C and 24-28 was repeated with various blends of compounds as described below.

Additives

(i) A L-Tyrosine B L-Methionine

(ii) C Tris (hydroxymethyl) methylammonium hydrochloride

(v) D Corrosion inhibitor N-2 aminoethyl-2-oleyl-imidazoline

(v) E alkyl benzyldimethyl ammonium chloride sold by Hoechst under the Trade Mark DODIGEN 5462 as a corrosion inhibitor.

Vinyl Polymer

PVP Polyvinyl pyrrolidone of Molecular Weight (Mw) about 700,000 (from BDH Ltd)

The results were as follows, with an averaged inhibition time from several experiments.

Example	Additive (ppm)		PVP Amount (ppm)	pH	Inhibition Time (min)
29	C345	D39	381		390
30	C356	D25	600	4.5	189
31	A314	D39	608	11.3*	230
32	A351	D156	607	4.3	38
33	B344	D31	614	11.3*	106
34	C356	E50	600	5.3	534
35	C356	-	600	5.3	80

*Denotes pH adjusted with concentrated aqueous ammonia.

Examples D and 36-39

To assess the efficiency of ice inhibitors suitable for use in the method of the présent invention, tests were carried out using the following procedure:

Six plastic pots, each containing a stirring paddle and a thermocouple for temperature measurement, were placed in a cooling bath. The bath itself had two thermocouples and two additional stirrers to ensure even mixing. All the thermocouples were connected to a Magus data logging system.

Test solutions were prepared in 100 ml flasks, a 1% solution being equivalent to a 1 g of active compound in 100 ml water. Thus 1 ml of a 1% solution in 100 ml water gave a concentration of 100 ppm.

The test solutions were prepared from twice distilled water and placed together with 1 g of Ballatini into each pot. Two of the pots contained water without any inhibitor chemical for reference.

The test solutions were stirred with the cooling bath kept at -2°C throughout and the time for ice formation to occur monitored by the data logging system.

The results are given in the Table which clearly shows the ice inhibiting effect of the chemicals tested.

Example	Inhibitor	Concentration	Time for Ice Formation
		ppm	hrs*
D	Deionized water	-	1
36	(+-)2-cis, 4-trans abscisic acid	200 400	48+ 48+
37	L-lysine	400	12.2
38	Glycine	400	6.9
39	DL-lysine	400	5.3

* represents the mean duration based on several test runs.

Example 40

The inhibitor blend of Example 34 was tested in a field trial in the North Sea. A wet gas line comprised water and natural gas, which was put "in mole %" carbon dioxide 0.59%, nitrogen 1.08%, methane 93.89%, ethane 3.49%, propane 0.57%, isobutane 0.1%, butane 0.12% and C_5+ hydrocarbons remainder. The gases were at 12.2°C (54°F) and 6.13MPa (890psi) and passed through a valve which could be partly closed to a fixed position, resulting in extra cooling which gave solid gas hydrates in the absence of added inhibitors; formation of hydrates was shown by an increase in the back pressure in the line up stream of the valve.

Into the gas line with the valve open was added continuously for 1hr an aqueous solution of Additive E. Then the blend of Example 34 was injected continuously at 500ppm total level, following which the valve was partly closed to the fixed position, and the upstream pressure watched. After 5hr, the pressure started to rise. After reopening the valve and dispersion of hydrates the pressure returned to the previous value.

The trial was then repeated with 1000ppm of the blend injected continuously; no pressure increase was observed over 14hr, so the level of continuously injected inhibitor was then reduced to 750ppm, resulting in no pressure increase over the next

4hr, and then reduced further to 600ppm with still no increase in pressure after a further 6hr while the blend was added. The injection of inhibitor was then stopped. After 5hr the upstream pressure started to rise denoting restart of gas hydrate formation; addition of methanol resulted 1 min later in onset of a reduction of the extra pressure.

Claims

1. A method for inhibiting or retarding hydrate or ice formation, which method comprises adding an additive (hereinafter called the Additive) which is at least one of (i) an amino acid or derivative thereof, (ii) an amino alcohol or derivative thereof, (iii) a glycol ether or derivative thereof (iv) a hydroxy acid or a derivative thereof, and (v) a corrosion inhibitor, the Additive being added in an amount effective to inhibit or retard hydrate or ice formation, to a medium susceptible to hydrate or ice formation, with the proviso that Additives (i) which are of Formula II, are not added as sole Additives or in admixture as sole other Additive with Additive (v).

2. A method according to claim 1 wherein the Additive is water soluble.

3. A method according to claim 1 or 2 wherein the Additive (i) is tris N-hydroxymethyl glycine or an alpha amino acid of formula $R\text{-}CH(NH_2)CO_2H$, wherein R represents an alkyl, hydroxyalkyl, alkoxy-alkyl, mercapto alkyl (or corresponding disulphide) or alkyl mercapto alkyl group.

4. A method according to claim 1 or 2 wherein the Additive is a hydroxy primary amine, preferably trihydroxymethyl-methylamine.

5. A method according to claim 1 or 2 wherein the Additive is a glycol ether which is derived from a diol or self condensate thereof with one hydroxyl group etherified, or an acyl derivative of such a glycol ether.

6. A method according to any one of claims 1-5 wherein an

Additive comprises a corrosion inhibitor, which is a quaternery ammonium salt, a long chain aliphatic hydrocarbyl N-heterocyclic compound or a long chain amine.

7. A method according to any one of claims 1-6 wherein the Additive comprises Additive (v) and at least one of (i)-(iv).

8. A method according to any one of claims 1-6 wherein the Additive comprises at least one polymer of a polar ethylenically unsaturated compound.

9. A method according to claim 8 wherein said unsaturated compound contains an N-heterocyclic group.

10. A method according to claim 8 or 9 which comprises adding Additive (v), at least one of i-iv and said polymer.

11. A method according to any one of claims 1-10 wherein the Additive concentration is 30-10,000ppm, based on the total water content of the medium.

12. A method according to any one of claims 1-11 wherein the amount of methanol, ethanol, or mono, di or triethylene glycol (if any) present relative to the total water volume in the medium is less than 5%.

13. A method according to any of claims 1-12 wherein the Additive ( ) retards or inhibits formation of lower alkane hydrates.

14. A method according to any of claims 1-12 wherein the Additive(s) retards or inhibits formation of ice.

15. An inhibitor formulation comprising a mixture of at least 2 Additives (i)-(v) each of which is as defined in any one of claims 1-7.

16. A formulation according to claim 15 which also comprises a polymer as defined in claim 8 or 9.

17. An oil based drilling mud comprising at least one Additive (i)-(v) as defined in any one of claims 1-7.

18. Use of an Additive as defined in any one of claims 1-7 or formulation according to claims 15 or 16 in the transportation of fluids comprising gas and water.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 94/00757

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 E21B37/06 C10L3/00 C09K7/06 F17D1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C10L E21B C09K F17D F15D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 323 775 (I.F.P.) 12 July 1989 see the whole document ---	1,2,5, 11-13,18
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P,X	EP,A,0 536 950 (THE BRITISH PETROLEUM COMP.) 14 April 1993	1,2,7, 11-13, 15,18
Y	see the whole document --- -/--	7,10,15, 16

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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